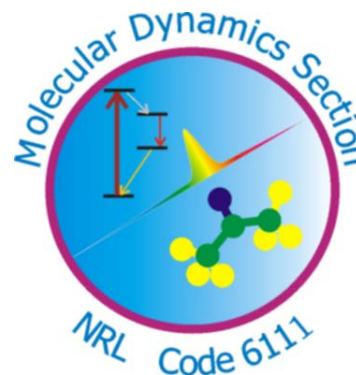

Photochemistry of $\text{Mn}_2(\text{CO})_{10}$ with 400 nm Excitation Studied by Ultrafast Time-Resolved IR Spectroscopy



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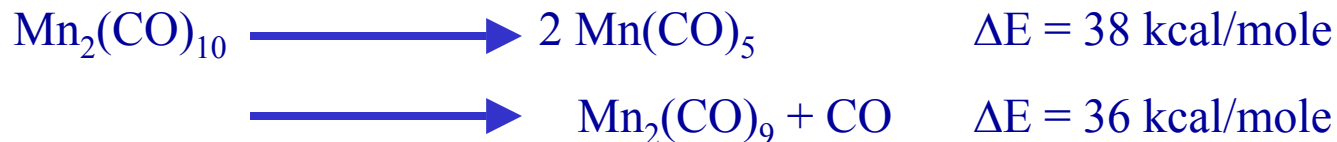
Introduction

What mechanisms mediate physical processes in the condensed phase? How?

- Photochemistry
 - . Branching Ratio
- Vibrational relaxation
 - . Rate, Pathway
- Effect of Solvent

Why $\text{Mn}_2(\text{CO})_{10}$?

$\text{Mn}_2(\text{CO})_{10}$ photodissociates via two channels:



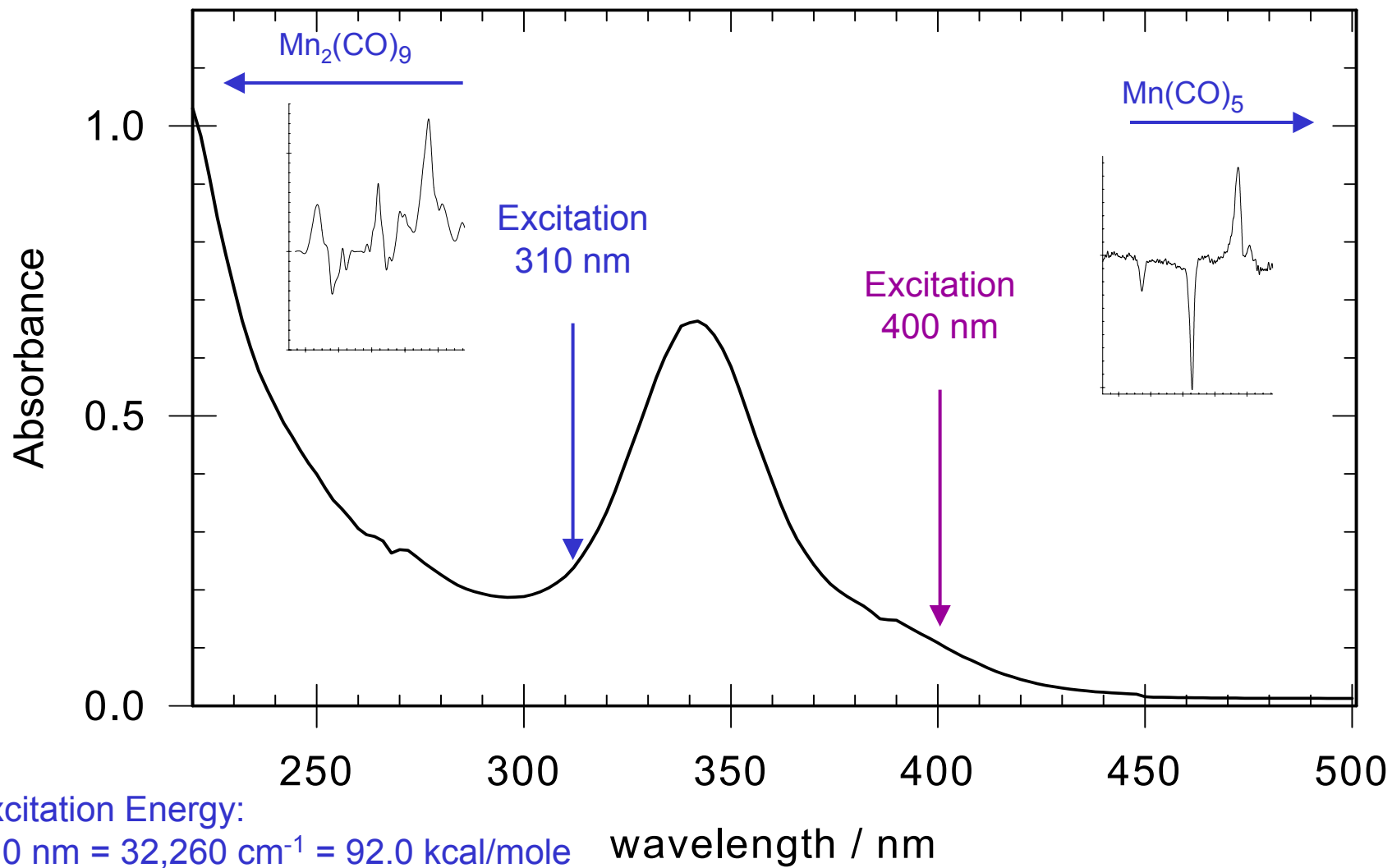
In this study, we examine the solvent dependence of vibrational relaxation for a single metal carbonyl photoproduct after photodissociation.

Introduction (cont.)

Historically, two general classes of experiments

- Long Time Product Detection
- Time-Resolved Detection
- Time-Averaged or Product Detection for $\text{Mn}_2(\text{CO})_{10}$
 - Distinct visible bands assigned to products
 - 800 nm for $\text{Mn}(\text{CO})_5$, 500 nm for $\text{Mn}_2(\text{CO})_9$
 - Branching ratios
 - More $\text{Mn}_2(\text{CO})_9$ at shorter excitation wavelengths
 - IR spectra of both parent molecule and products
 - Parent and product bands are well separated in IR

UV/VIS Spectra of $\text{Mn}_2(\text{CO})_{10}$



Excitation Energy:

310 nm = $32,260 \text{ cm}^{-1}$ = 92.0 kcal/mole

400 nm = $25,000 \text{ cm}^{-1}$ = 71.3 kcal/mole

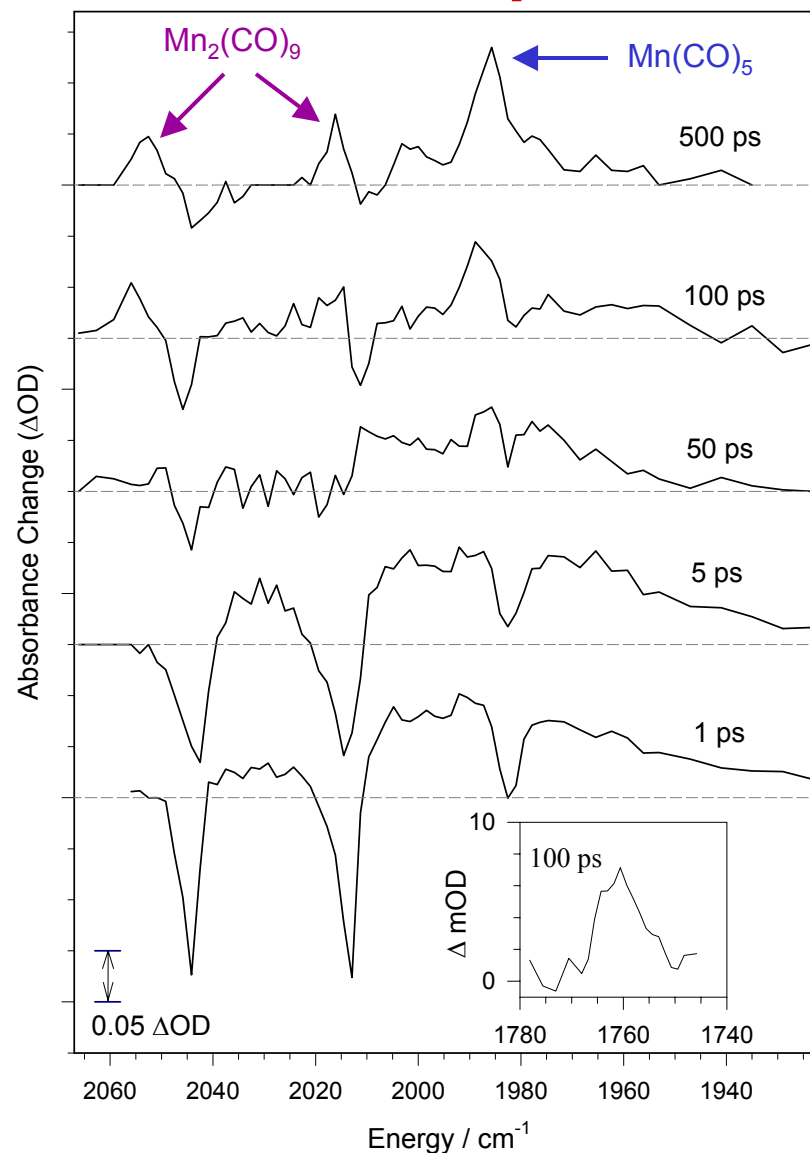
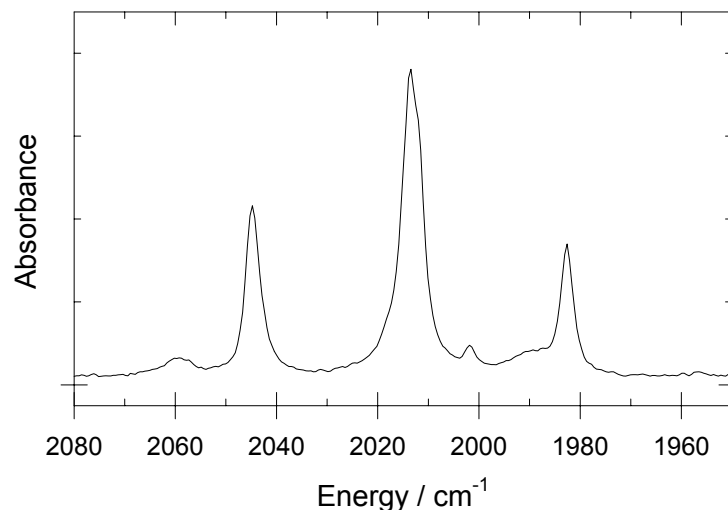
$\text{Mn}_2(\text{CO})_{10}$ Overview

- Time-Resolved Detection for $\text{Mn}_2(\text{CO})_{10}$ and other $\text{M}(\text{CO})_n$'s
 - Photodissociation
 - . 308 nm / VIS
 - Waldman et al., 2 ps formation time for $\text{Mn}_2(\text{CO})_9$ products.
 - Geminate recombination
 - . 295 nm / VIS
 - Zhang and Harris observed two distinct recovery channels for $\text{Mn}_2(\text{CO})_9$ in CH: 15 ps, 170 ps, somewhat faster in i-PrOH.
 - . 295 nm / IR
 - Yang et al., $\text{Re}_2(\text{CO})_{10}$, biexponential decays, 50 and 500 ps time scales.
 - Vibrational relaxation
 - . 310 nm / IR
 - Owrutsky and Baronavski, 30 - 55 ps growth/VER time for $\text{Mn}_2(\text{CO})_9$.
Congested IR spectrum.
 - Bridge formation in $\text{Mn}_2(\text{CO})_9$.

310 nm Excitation IR Time Resolved Spectra

- Transient bleaches from parent
- Broad initial transient absorption
- Both $\text{Mn}_2(\text{CO})_9$ and $\text{Mn}(\text{CO})_5$ products observed.
- Both terminal and bridging $\text{Mn}_2(\text{CO})_9$ observed.

FTIR Spectrum of $\text{Mn}_2(\text{CO})_{10}$



400 nm Excitation

Congested using UV excitation, time-resolved IR spectra limits ability to extract dynamical information.

- Several photoproducts in addition to parent molecule
- Decreasing excitation wavelength favors $\text{Mn}_2(\text{CO})_9$ production.
- UV excitation at 310 nm produces, $\Phi(\text{Mn}(\text{CO})_5) / \Phi(\text{Mn}_2(\text{CO})_9) = 0.25$.

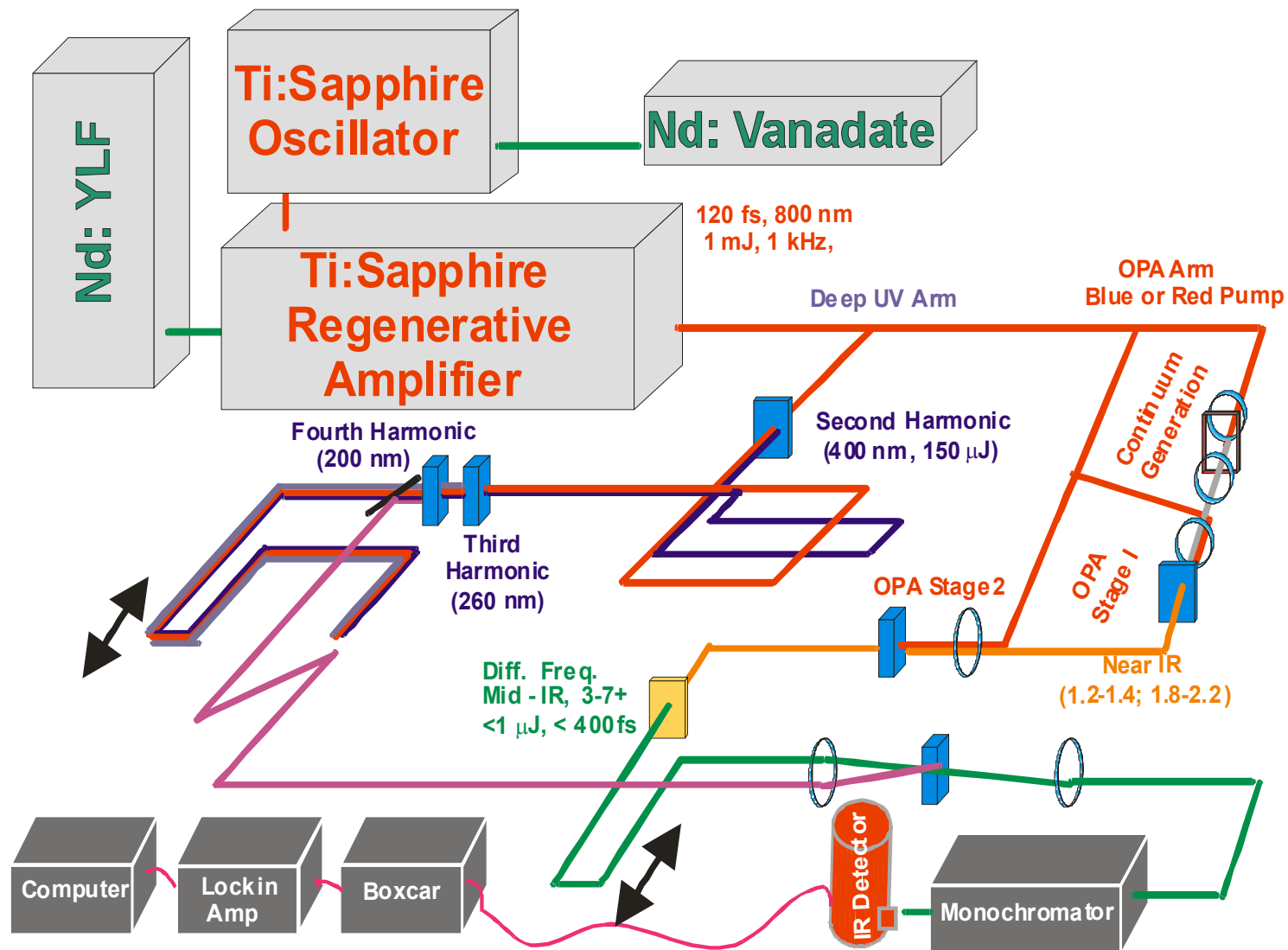
Some evidence of solvent-dependent dissociation dynamics

- $\text{Mn}_2(\text{CO})_9$: 15 and 170 ps in CH vs. 10 and 145 ps in i-PrOH
Zhang and Harris
- $\text{Rh}(\text{CO})_2(\text{acac})$: 20 ± 4 ps for CCl_4 vs. 5 ± 1 ps for *n*-hexane
Dougherty et al.

400 nm excitation

- Extrapolation of $\Phi(\text{Mn}(\text{CO})_5) / \Phi(\text{Mn}_2(\text{CO})_9)$ to 400 nm indicates a ratio of 2 – 4.

Femtosecond Deep UV - Mid IR Laser System



Time-Resolved IR Spectra

$\text{Mn}_2(\text{CO})_{10}$ in cyclohexane

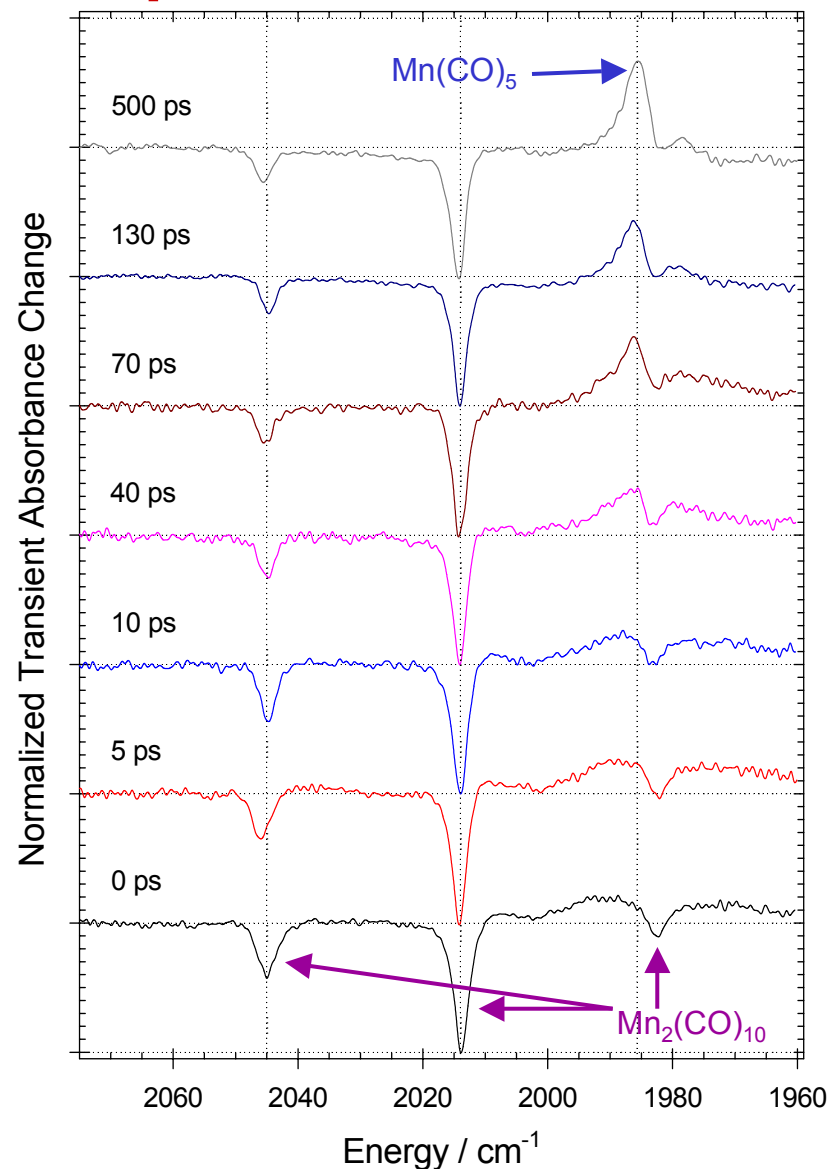
- 3 Transient Bleaches

- 2045, 2014, 1983 cm^{-1}
- 20 – 70 mOD
- 2 – 5 cm^{-1} FWHM

- 1 Transient Absorption

- 1985 cm^{-1}
- 25 cm^{-1} FWHM initially
- 40 mOD at long time

Initial, broad absorption is smaller than for 310 nm excitation.

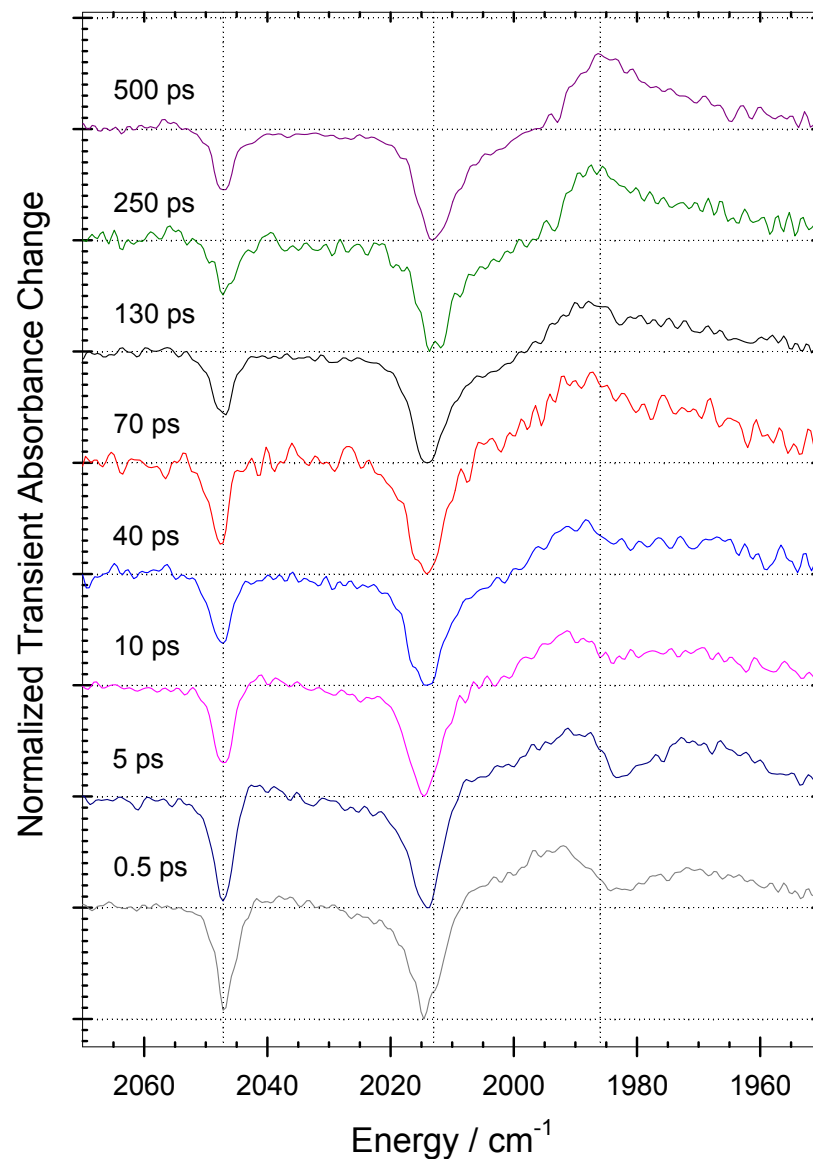


TR IR Spectra (cont.)

$\text{Mn}_2(\text{CO})_{10}$ in isopropanol

- 3 Transient Bleaches
 - 2047, 2013, 1983 cm^{-1}
 - 15 – 35 mOD
 - 4 – 8 cm^{-1} FWHM
- 1 Transient Absorption
 - 1985 cm^{-1}
 - 40 cm^{-1} FWHM initially
 - 25 mOD at long time

Static ΔA 's scale with solvent, consistent with behavior of parent molecule.



Some Experimental Details of TR IR Spectroscopy

Vibrational coherence

- Well documented in literature for ultrafast IR detection and have little impact on this work due to disparate timescales.

Polarization Anisotropy

- For parallel pump and probe polarizations (perpendicular to molecular axis), 2014 cm^{-1} transition does not decay.
- For perpendicular pump and probe polarizations (probe parallel to molecular axis), 2045 and 1983 cm^{-1} transitions do not decay.
- Consistent with calculated symmetry and transition moment directions of the electronic and vibrational bands of the ground state parent molecule.

Product Vibrational Relaxation Analysis

How to approach analysis?

- Absorption is a collective result from a high number of:
 - Hot bands
 - Vibrational states with anharmonic shifts
- Assuming internal energy redistributes faster than vibrational relaxation
 - Relaxation / Cooling can be monitored via absorption width
 - $\Delta T \rightarrow \Delta \nu$


Product Band Narrowing

- Simplified approach following Dougherty et al.
- Each spectrum is fit as a linear combination of line shapes
 - Lorentzian line shape for bleaches
 - Gaussian line shape for absorptions

Product Band Narrowing Analysis (cont.)

Bleach

Absorption

$$A(\nu) = \sum_{i=1}^3 \frac{\Delta A_{oi}}{1 + \left(\frac{\nu - \nu_i}{\Delta \nu_i / 2} \right)^2} + \Delta A_{o,abs} e^{-\left(\frac{\sqrt{2(\ln(2))}(\nu - \nu_{abs})}{\Delta \nu_{abs}} \right)^2}$$


The individual values for $\Delta \nu_{abs}(t)$ from the fit are used collectively to determine the effective relaxation / cooling times for $\text{Mn}(\text{CO})_5$ in CH and i-PrOH.

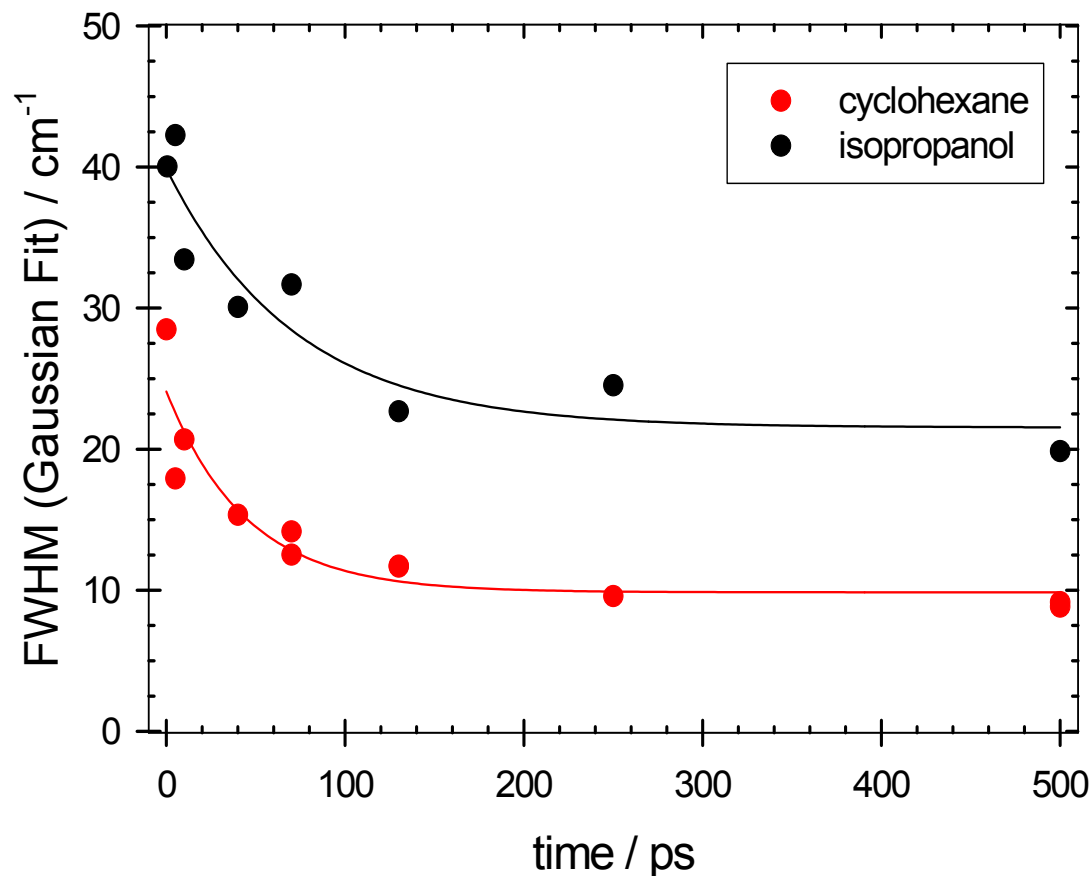
$$\Delta \nu_{abs}(t) = \left[\left(A \exp^{-t/\tau} + \Gamma \right)^2 + (IRF)^2 \right]^{0.5}$$

Measured	Known	Extracted
$\Delta \nu_{abs}$ = Absorption width	Γ = Static abs. width IRF = Instrument funct.	A = Additional width τ = VR time

Narrowing Analysis Results

Vibrational relaxation fitting parameters for $\text{Mn}_2(\text{CO})_{10}$ in CH and *i*-PrOH.

	CH	<i>i</i> -PrOH
A / cm^{-1}	14.2 ± 2.0	18.4 ± 3.2
τ / ps	44.7 ± 17.4	71.7 ± 34.5
Γ / cm^{-1}	9.8 ± 1.3	21.5 ± 2.6



A and τ do not depend on solvent!

Results

VR rate for $\text{Mn}(\text{CO})_5$ for 400 nm excitation in two solvents

- CO – stretch modes not excited in product
 - UV/VIS experiments found that for $\text{M}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), excited bands would shift 10 – 20 cm^{-1} .
 - IR/IR experiments on similar modes in $\text{M}(\text{CO})_6$ suggest that for CO-stretches, relaxation times are longer than 100 ps.
- We find
 - VR time of 60 ps for both solvents
 - Photodissociation-induced additional width is the same for both solvents, 16 cm^{-1}
 - Branching ratio $\Phi(\text{Mn}(\text{CO})_5) / \Phi(\text{Mn}_2(\text{CO})_9) \geq 2.5$

Lessons from 400 nm

- What governs VR & energy disposal in this system?
 - Excess energy has little effect
 - VR rates are not appreciably slower with 400 nm excitation than with UV excitation.
 - Type of product mode excited is an important factor
 - CO-stretch modes are not excited in product.
 - Low frequency modes are the pathway for VR.
 - Solvent has little effect on VR
 - Measured for two solvents, CH and i-PrOH.
 - VR-related properties are not affected by changing solvent.

Smaller and Smaller

The objective of our program is to examine the spectroscopy and dynamics of small molecules in confined spaces such as at chemical interfaces. Deep UV (DUV) excitation typically required.

Why small molecules?

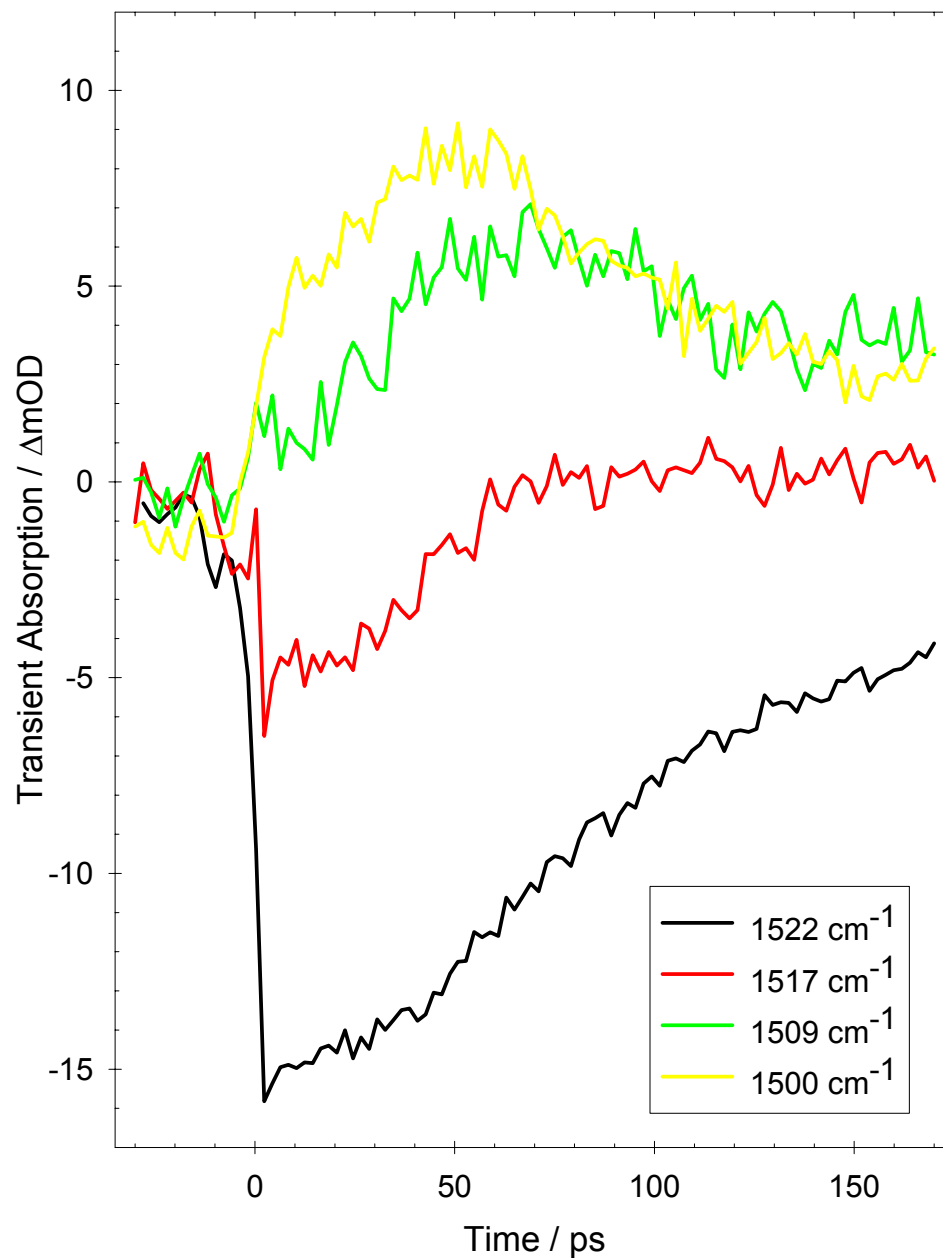
- More detailed / gas phase literature to drawn upon
 - . Good connection to theory
- Less perturbation to system under study
 - . Example: reverse micelles
- Two examples:
 - CS_2 in CD_3OD
 - $\text{Na}_4\text{Fe(II)(CN)}_6$ in H_2O

CS_2 in CD_3OD

200 nm pump / IR probe in 50 μm jet.

Geminate recombination

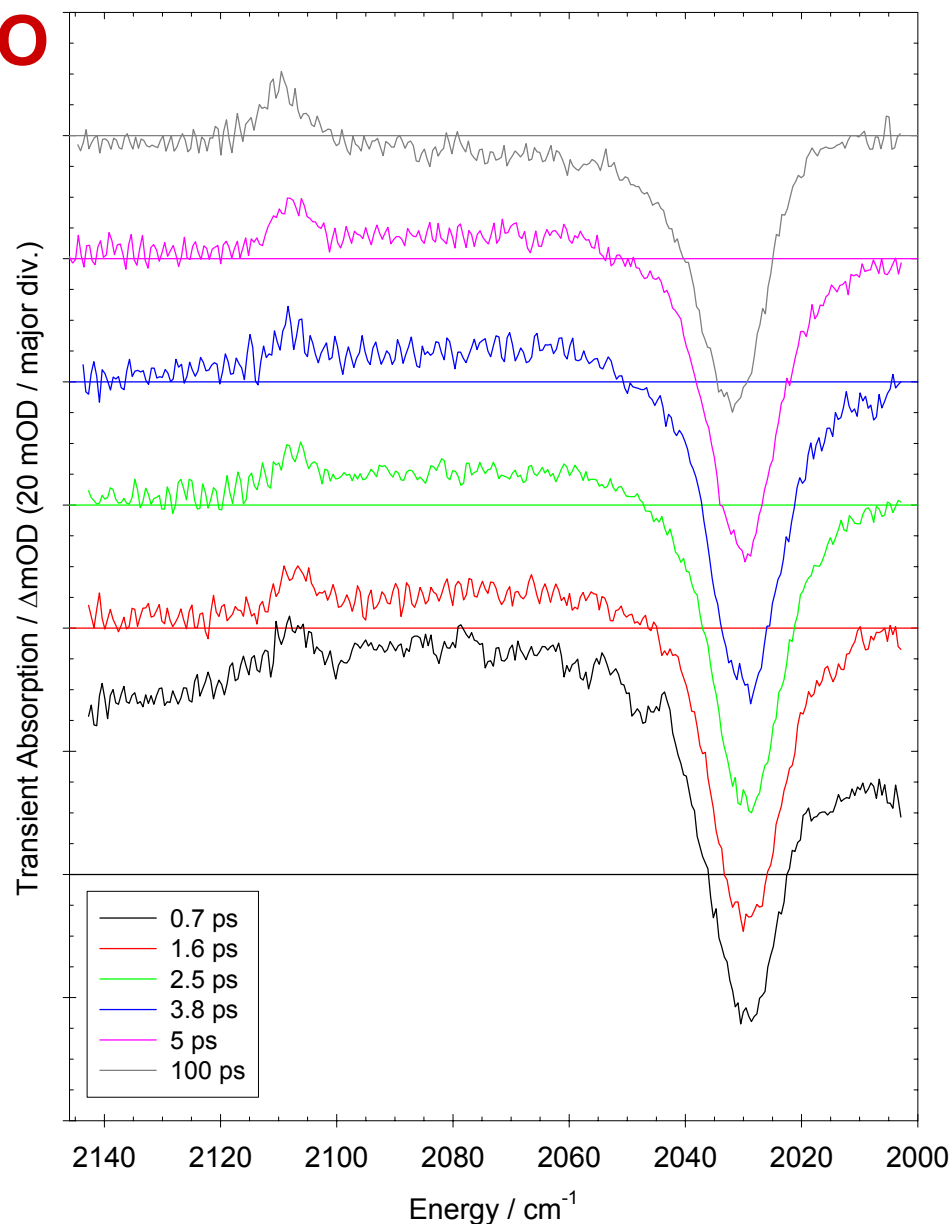
Similar time scale as seen by Keiding et al. for 200 nm / UV pump – probe studies.



$\text{Na}_4\text{Fe(II)(CN)}_6 \cdot 3\text{H}_2\text{O}$ in H_2O

200 nm pump / IR probe in 300 μm jet.

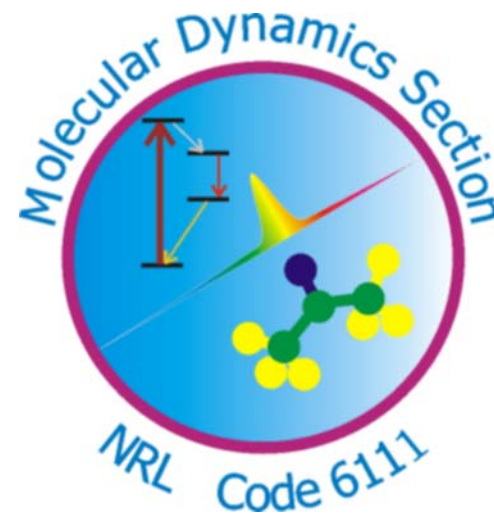
- Broad absorption at early time due to electrons. Decays with 1.6 ps.
- Rapid growth of Fe(III)(CN)_6 product at 2105 cm^{-1} on our time scale.
- Our decay time for the trapped electrons is somewhat longer than those seen by Lian and coworkers and Bradforth and coworkers.



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Presentation:

<http://chem1.nrl.navy.mil/dan/icp02>